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Performance of surfactant-modified forms of clinoptilolite and pumice in nitrate removal from aqueous solution

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ABSTRACT

Clinoptilolite and pumice are both natural, low-cost and available sorbent materials. In this study, surfactant-modified forms of clinoptilolite (SMC) and pumice (SMP) using hexadecyltrimethylammonium bromide were used for the removal of nitrate from aqueous solutions. Batch experiments were performed to investigate the effects of factors including pH (2–10), contact time (10–180 min), adsorbent dosage (0.1–1.5 g/L) and nitrate initial concentration (30–200 mg/L) on the sorption performance. Both natural and modified forms of sorbents were characterized by X-ray fluorescence, scanning electron microscopy and Brunauer–Emmett–Teller techniques. The optimal experimental condition for both adsorbents were pH = 5, contact time = 30 min and adsorbent dose = 0.5 g/L. The equilibrium isotherm data were well described using the Langmuir model ($R^2 = 0.99$) with a monolayer sorption capacity of 30.2 and 27.6 mg/g for SMC and SMP, respectively. The adsorption kinetic for nitrate sorption followed the pseudo-first-order model. Results of the regeneration study showed that both sorbents could be reused for nitrate removal in several cycles. The study revealed the SMC and SMP both could be used as efficient and inexpensive materials for nitrate removal from aqueous solutions.

Keywords: Adsorption; Modified clinoptilolite; Modified pumice; Nitrate removal

1. Introduction

Many organic and inorganic anions identified in water resources are potentially dangerous. The anionic pollutants that originated from the production of chemicals and synthetic compounds have raised public concerns about the quality of water [1].

In recent decades, agricultural and industrial activities and municipal wastewaters have been the main sources of excessive nitrogen in water resources [2]. Although nitrogen is an essential nutrient for living organisms such as animals, plants and other ecosystems, its high concentration in drinking water can be toxic and carcinogenic for consumers [3]. High concentrations of nitrate in drinking water is dangerous because of the reduction of nitrate to nitrite, and its combination with hemoglobin for methemoglobin formation in the blood; also, nitrate may increase the potential for nitrosamine formation which its carcinogenic effects are well documented [4,5].

Nitrogen species in the form of nitrite, nitrate, nitrous oxide and nitric oxide are soluble in water and are found in both surface and groundwater resources [6]. Furthermore, the presence of additional nitrogen in an aquatic environment can lead to eutrophication [7,8]. Nitrate contamination

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of groundwater resources is a global problem and has been reported in many parts of the world [9].

Many methods are available to remove nitrate from water, including biological denitrification, ion exchange, reverse osmosis, electrolysis, precipitation, adsorption and reduction [10–14]. Many of these processes are not completely effective and not cost-effective technologies. Besides the inadequacy of conventional technologies for nitrate removal, the adsorption process is currently considered as the easiest and a cost-effective method for water and wastewater treatment [11]. Activated carbon, zeolite, clay minerals, biomaterials, conventional and non-conventional materials have been extensively used as effective adsorbents for the removal of pollutants from water and wastewater [14–19]. Mineral clays can be used as adsorbent due to their natural availability, abundance and their physicochemical characteristics such as high specific surface area and high cation-exchange capacity (CEC) [20,21]. Among clays, natural zeolite and pumice have been used with a variety of usages in the adsorption process as low cost and effective sorbents for the removal of pollutants from water and wastewater.

Natural zeolites are one of the most important porous minerals formed by hydrated aluminosilicates [22,23]. Clinoptilolite is the most common mineral amongst zeolitic materials which has valuable properties, including large specific surface area, porous structure and high CEC [24]. Another worthwhile natural mineral clay is pumice. The pumice has a crystalline porous and lightweight structure, formed by the exhaust of gases during the process of solidification of lava. This natural sorbent is valued for many physical and chemical benefits such as; large surface area, high porosity, small particle size and high CEC [25]. Because of these characteristic properties, the natural zeolite and pumice both may be used as natural adsorbents for the removal of pollutant compounds such as phenol, oils, copper, nickel, and phosphorus. Owing to the many advantages of these sorbents, pumice has excellent adsorption capacity and can be easily modified [26,27].

Although these clays are widely distributed in different regions of Iran, where the raw natural materials have been widely used for environmental remediation, they are unable to remove anions for aqueous solutions and usually have little affinity for anions [28]. However, the sorption capacity of anions by these natural sorbents may be increased through modification of them using cationic surfactant species such as hexadecyltrimethylammonium bromide (HDTMA-Br) [29]. Recently, various studies demonstrated the utilization of modified natural zeolitic materials for the removal of different pollutants [30–33]. In our previous works, modified zeolite was used for fluoride removal from aqueous solutions [34]. To the best of our knowledge, no investigation on both modified clinoptilolite and pumice with a surfactant, for nitrate removal has been reported.

In this paper, we compared the capability of modified clays in the removal of nitrate from water. The nobility and main goals of this study are:

- To evaluate the nitrate removal by bilayer surfactant-modified clinoptilolite (SMC) and pumice (SMP), using a batch adsorption study.
- To provide more information on the ability of nitrate adsorption by modified clinoptilolite and pumice.
- To indicate the difference between these two natural adsorbents in the removal of nitrate from water.
- Consequently, by comparing the capability of these modified clay, this study presents some idea of adsorbents effectiveness.

In the following sections, the modified clinoptilolite and pumice will be known as SMC and SMP, respectively. The impacts of variables including pH, contact time, adsorbent dosage and initial concentration of nitrate will be discussed. Moreover, many equilibrium and kinetic models will be applied to describe the sorption process.

2. Materials and methods

2.1. Chemicals

Natural Iranian clinoptilolite-rich zeolitic tuff and pumice stones were provided from South Semnan and East Azerbaijan, respectively. All chemicals including sodium nitrate and HDTMA-Br were of an analytical grade and obtained from Merck Company (Germany).

2.2. Pre-treatment of clinoptilolite and pumice by salt

To increase the CEC, natural clinoptilolite and pumice were agitated for 24 h with 1 mol NaCl solution. Then to convert the samples to a sodium form they were completely washed by distilled water until becoming free of chloride ion (using $AgNO_3$-based colorimetric method) and were dried at 80°C for 24 h [31].

2.3. Treatment of clinoptilolite and pumice with surfactant

The SMC and SMP were prepared according to the method in our previous work [31]. 30 g of each clay was mixed with 180 mL of HDTMA solution (60 mmol/L) at 25°C and stirred for 24 h. The supernatant was then passed through a Whatman Paper No. 1. Then the paper was washed several times by distilled water and dried at 80°C for 24 h. From this step, the modified clinoptilolite and modified pumice were known as SMC and SMP, respectively.

2.4. SMC and SMP characterization

The mineral contents of natural and modified clinoptilolite and pumice were determined based on the X-ray fluorescence (XRF) technique by PW2404 X-ray spectrometer (Table 1). The textural and internal characteristics including specific surface area, average pore diameter, and pore volume distribution were analyzed using Brunauer–Emmett–Teller method (Belsorp Mini2, Japan) (Table 2). The internal and external surface morphology of natural and modified clays were inspected by scanning electron microscopy (SEM, XL30 Philips Company, The Netherlands) (Fig. 1).

2.5. Adsorption kinetics

The study of adsorption kinetics is important to evaluate the rate of the sorption process. The kinetic models

Table 1
Physico-chemical properties of natural and modified clinoptilolite and pumice

Composition (WT %)	SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	MgO	CaO	P_2O_5	SO_3
Natural clinoptilolite	68.61	9.85	3.61	3.727	1.02	0.507	1.3	0.023	0.12
SMC	64.06	9.33	2.24	3.563	0.86	0.727	0.63	0.028	0.17
Natural pumic	70.94	6.86	5.415	0.973	3.988	0.141	6.76	1.47	<0.0005
SMP	65.87	5.32	1.29	1.16	3.42	1.04	4.21	0.37	0.17

Table 2
Textural characteristics of natural and modified clinoptilolite and pumice

Adsorbent	Pore volume (cm^3/g)	Average pore diameter (nm)	Surface area (m^2/g)
Natural clinoptilolite	0.051	26.66	13.7
SMC	0.032	27.8	13.5
Natural pumic	4.3	26.74	6.46
SMP	4.79	19.6	9.79

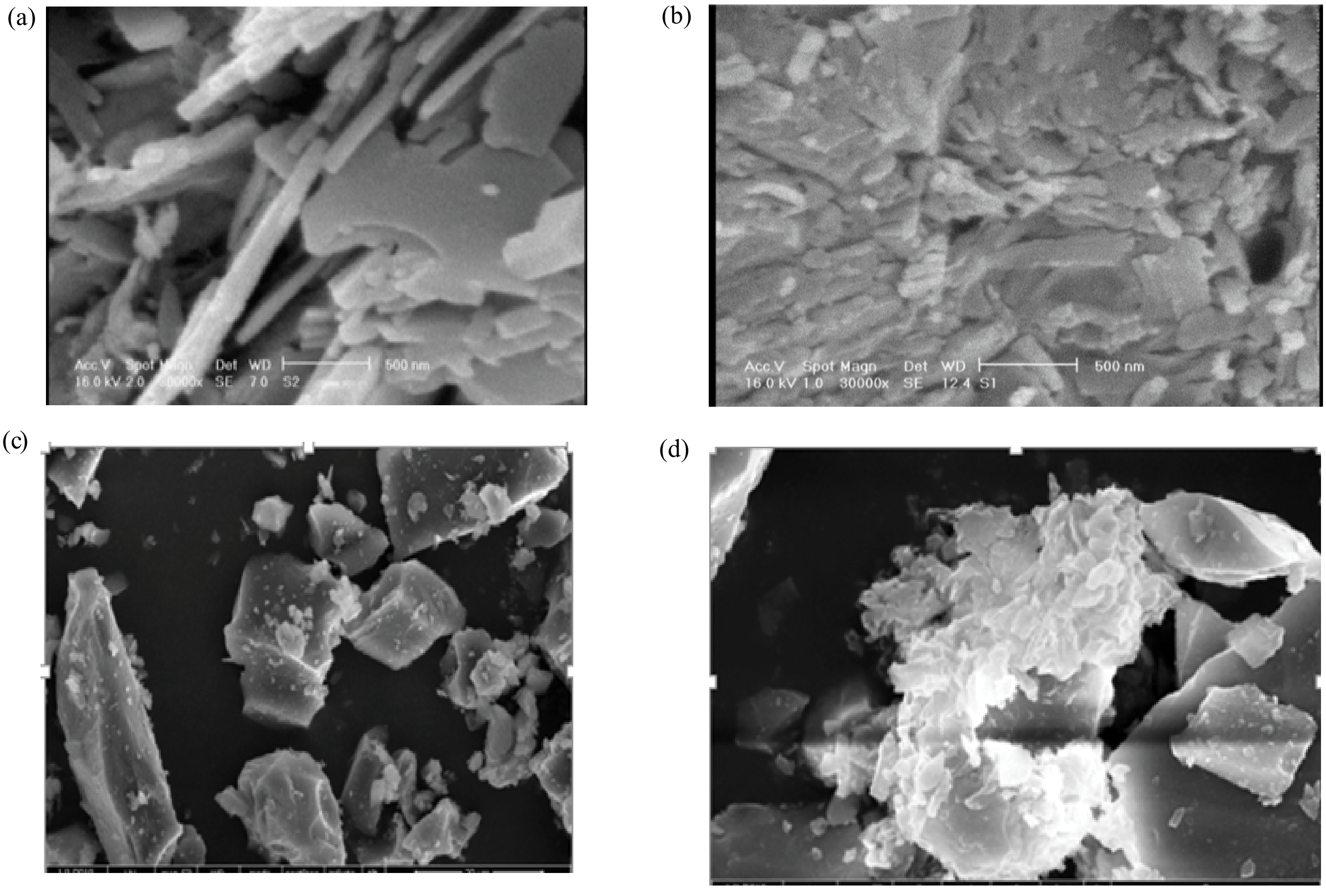

Fig. 1. SEM images of (a) natural clinoptilolite, (b) modified clinoptilolite, (c) natural pumice, and (d) modified pumice.

including pseudo-second-order [35] and Lagergren pseudo-first-order [36] were applied to the kinetic data.

The non-linear form of Lagergren pseudo-first-order and pseudo-second-order equations are represented by Eqs. (1) and (2), respectively, as follows:

$$q_t = q_e - \exp\left(\ln q_e - k_1 t\right) \tag{1}$$

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \tag{2}$$

where q_e (mg/g) and q_t (mg/g) are the sorption capacity at equilibrium condition and at time t, respectively. k_1 (1/min) and k_2 (g/mg min) are the kinetic rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

The adsorption kinetics for SMC and SMP were studied by applying a contact time from 0 to180 min, with an initial nitrate concentration of 100 mg/L at pH = 5 and a sorbent dose of 0.5 g/L.

2.6. Equilibrium experiments

All of the nitrate sorption batch experiments were implemented on a shaker, operated at 120 rpm. Every batch flask contained 50 mL of nitrate solution with an initial concentration of 30–200 mg/L. The initial pH solution was adjusted to 5 using 0.1 N HCl and NaOH solutions. Then, 0.5 g of sorbent was added to each flask and the suspension was shaken for 180 min at laboratory temperature. The solutions were then analyzed for nitrate after passing through a paper filter (0.45 μm). Removal efficiency and adsorption capacity of nitrate were calculated using the following equations:

$$\text{Nitrate removal }\left(\%\right) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{3}$$

$$q_e = \frac{\left(C_0 - C_e\right)V}{W} \tag{4}$$

where q_e is the adsorption capacity (mg/g) at equilibrium condition, C_0 and C_e are the initial and equilibrium nitrate concentrations (mg/L), V is the volume of the nitrate solution (L) and W is the mass of the adsorbent.

The nitrate removal capacity of SMC and SMP were studied at variable conditions of pH (2–10), adsorbent dose (0.1–1.5 g/L), contact time (10–180 min) and initial nitrate concentration (30–200 mg/L). The pH_{ZPC} for SMC and SMP was measured after a contact time of 24 h with 0.5 g/L of the adsorbent by addition of 0.1 M HCl or 0.1 M NaOH solution to 100 mL of NaCl solution (0.01 M) as an electrolyte. The regeneration and reuse behavior of adsorbents in this section were examined by the batch method. The continual adsorption-regeneration cycle of SMC and SMP was carried out for five cycles. In the first cycle of nitrate regeneration, SMC and SMP adsorbents were washed by NaOH solution (50 ml of 0.1 mol/L) for several times and subsequently dried at 120°C for 24 h to remove the adsorbate from the surface. Then, 0.7 g of regenerated sample was contacted with an initial nitrate concentration of 70 mg/L for 120 min. The regenerated sorbents were used again in the subsequent experiments. The final concentration of Nitrate was determined using a UV/Vis Perkin Elmer (US), with detecting wavelength at 220 nm. The variables and experimental conditions are given in Table 3.

Langmuir and Freundlich isotherm models were used to describe the equilibrium condition of the sorption process. The Langmuir isotherm model is applicable for monolayer sorption on a homogeneous surface [37,38]. Non-linear form of Langmuir and Freundlich isotherm models are presented in Eqs. (5) and (6), respectively.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

$$q_e = k_f C_e^{\frac{1}{n}} \tag{6}$$

The substantial characteristics of the Langmuir isotherm can be explained by R_L as a separation factor or equilibrium dimensionless parameter [39] that interprets the type of isotherm as follows:

$$R_L = \frac{1}{1 + b C_0} \tag{7}$$

Equilibrium experiments were done at room temperature with 50 mL solutions of nitrate at different initial concentrations (30–300 mg/L) with a fixed dose of adsorbent (0.5 g/L) at an optimum pH of 5. The suspensions were analyzed for the residual nitrate after 2 h to reach the equilibrium condition.

3. Results and discussion

3.1. Physico-chemical properties and textural characteristics of SMC and SMP

The mineral structure and physicochemical properties of natural and modified clinoptilolite and pumice were distinguished using the XRF technique as summarized in Table 1. The concentration of ten main elements is explained as the weight percentage of oxides. The result showed that the structural parameters and crystallinity of the samples changed slightly after pre and post-treatment. The amounts

Table 3
Experimental runs

Variables experiments		pH	Dose (g/L)	Concentration (mg/L)	Contact time (min)
1	Effect of pH	2–10	0.7	70	90
2	Effect of dose	5	0.1–1.5	70	30
3	Effect of contact time	5	0.5	70	10–180
4	Effect of concentration	5	0.5	30–200	30
5	Adsorption isotherms	5	0.5	30–300	60
6	Adsorption kinetics	5	0.5	100	0–180

of SiO_2, Al_2O_3, CaO, Fe_2O_3, and K_2O have been decreased because of substitution with the cationic surfactant and Na cations. The main chemical constituents of SMC and SMP near the natural pattern of clinoptilolite and pumice were SiO_2 and Al_2O_3. The Si/Al ratio for natural zeolite and pumice indicated that cationic exchange sites (–Al–O(C^+)–Si–; C^+ = cation) on the surface could be used as selective adsorption cores for the surfactant sorption [23]. The amount of Al_2O_3 in the natural and modified of pumice was less than that of forms of clinoptilolite. The specific surface area, total pore volume and average pore diameter of natural and modified forms of clinoptilolite and pumice were determined. As shown in Table 2, after the modification, the specific surface area of the SMC was decreased while it was increased for SMP. The reason for the decrease and increase is probably related to the structure of these clays. The pore volume of natural and modified pumice due to a spongy structure is greater than the natural and modified clinoptilolite.

The internal and external surface morphology of natural and modified clinoptilolite and pumice are given in Fig. 1. The SEM image shows the characteristic surface of natural and modified samples with surfactants. As presented in Fig. 1b, an organic layer of surfactant has been formed on the surface of clinoptilolite by modifying the zeolite with a surfactant, which appeared as big agglomerates on the surface of SMC. Fig. 1c shows that natural pumice had a spongy surface with irregularly shaped particles. It is evident from Fig. 1d, that after the modification of pumice with the surfactant, its exterior surface will be covered by surfactant and the porous texture then can't be seen obviously.

3.2. Effect of initial pH of nitrate solutions

The zero point charge (pH_{zpc}) of the adsorbent surface is an important parameter for the removal of pollutants in the adsorption process [40]. As shown in Fig. 2a, the pH_{zpc} of SMC and SMP were found to be 7.4 and 6.8, respectively. These values of pH imply that the adsorbent surfaces are at a neutral condition for the charge. Consequently, at a pH ≤ 7.4 for SMC and pH ≤ 6.8 for SMP, the surface of the sorbent contained a combination of positive and neutral sites at acidic side of the zpc curve and a combination of negative and neutral sites at alkaline side of the zpc curve (pH > 7.4 and 6.8). The nitrate anion can be attracted by the positively charged sites of SMC and SMC surface at $pH < pH_{zpc}$. Therefore, the maximum removal capacity of the NO_3^- will be remarkable when the pH of the solution is below the pH_{zpc}.

The amount of anions removal heavily depends on pH [41]. Therefore, in the present study, the nitrate removal was examined in a pH range of 2–10 under the experimental condition shown in Table 3. As shown in Fig. 2b, the pH found to be a considerable parameter in the removal of nitrate for both adsorbents. The maximum adsorption capacity was observed at pH = 5, in which the removal efficiency was detected >95% for SMC and >91% for SMP, respectively. This observation can be explained by the high electrostatic interactions between nitrate anion in the solution and positive head groups of surfactants on the surface of SMC and SMP and also by the selectivity of SMC and SMP surface for nitrate uptake [42].

According to the results, at any pH, nitrate sorption by SMC was higher than that by SMP, which confirm the higher capacity of SMC for nitrate ion uptake from aqueous solution. By the way, the adsorption capacity can be decreased by increasing pH from 8 to 12 for both sorbents. This decrease may be due to the negatively charged surface of sorbents with a high Coulomb repulsion and also the competition of anions for the adsorption sites at alkaline conditions [42,43].

3.3. Effect of adsorbent dose

The effects of SMC and SMP doses on nitrate removal were examined under different experimental conditions. The results are summarized in Table 3 and Fig. 3. As shown, when the SMC or SMP dosage was increased in a range of 0.1–0.5 g/L, the nitrate removal efficiency increased from 57% to 92% and 49% to 88%, respectively, which can be related to the increase of the amount of available active sites and the increase in the accessibility of active binding sites on the sorbent surface [44]. However, a further increase in the dosage of both adsorbents from 0.5 to 1.5 g/L could not significantly increase the nitrate removal efficiency. The decrease in adsorption capacity could also be attributed to several factors including; (i) existence of unsaturated sites during the adsorption process, (ii) overlapping and obstruction of active sites, and (iii) occurrence of aggregation [45].

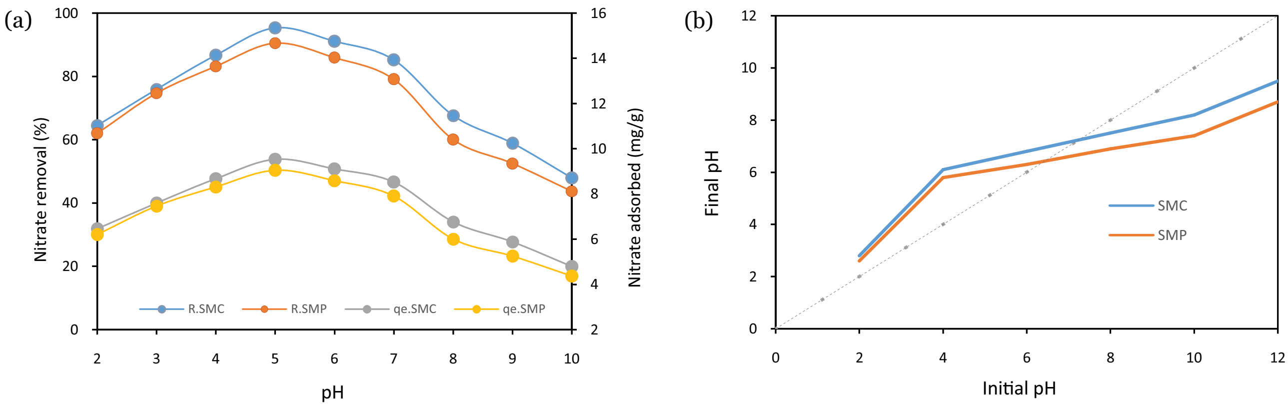

Fig. 2. (a) pH_{zpc} of ZMC and ZMP and (b) Effect of pH on nitrate removal efficiency.

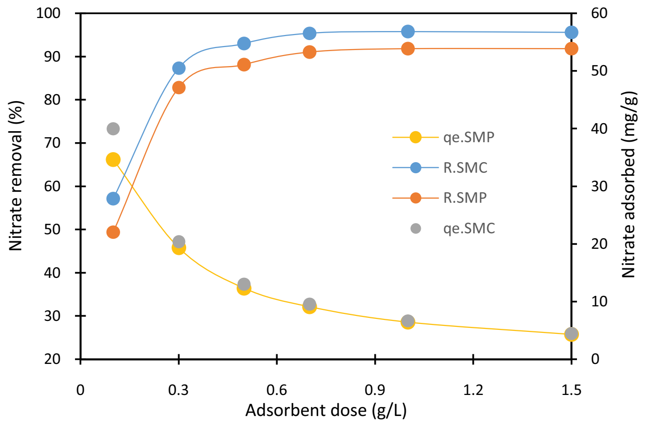

Fig. 3. Effect of adsorbents dose on nitrate removal efficiency.

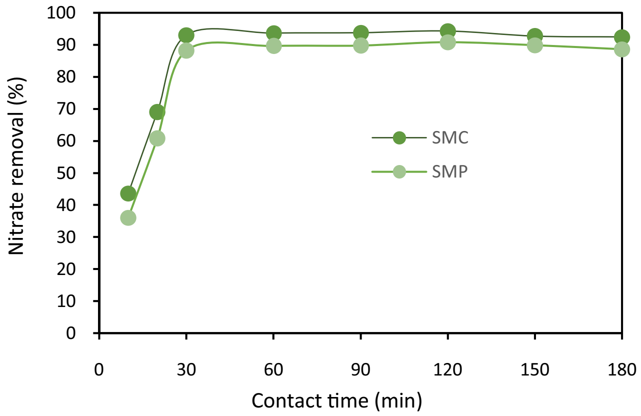

Fig. 4. Effects of contact time on nitrate removal efficiency.

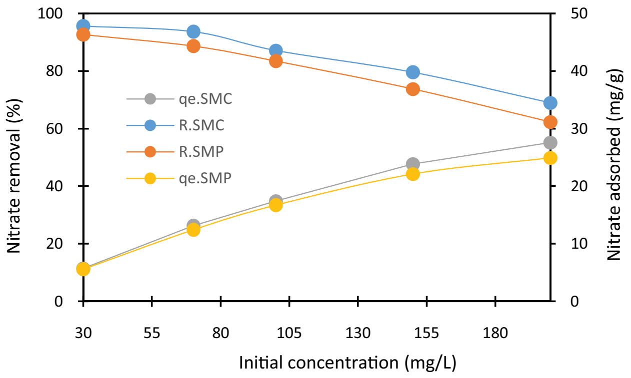

Fig. 5. Effect of initial concentration on nitrate removal.

Therefore, a dose of 0.5 g/L for both SMC and SMP was considered as the optimal adsorbent dosage for performing further experiments.

3.4. Effect of contact time

The duration of contact time between sorbent and sorbate is the most important factor can affect the efficiency of the sorption process [46]. The effect of contact time on nitrate removal by SMC and SMP was investigated in the range of 10–180 min under the condition summarized in Table 3. Fig. 4 clearly shows that the uptake of nitrate by SMC and SMP was increased over time to reach an equilibrium state after 30 min, then it remained constant with no significant increase in nitrate uptake. At the equilibrium condition, nitrate removal found to be 93% and 88% for SMC and SMP, respectively. This early obtained significant removal efficiencies may be due to the abundance inaccessible number of vacant adsorption sites at the first stage of the sorption process [44]. However, after equilibrium time the remaining sites may be unavailable due to repulsive forces between the nitrate ion and surface of the adsorbents [47].

3.5. Effect of nitrate concentration

The effect of initial nitrate concentration on adsorption efficiency by surfactant modified zeolite and SMP is shown in Fig. 5. With increasing nitrate concentration from 20 to 200 mg/L, nitrate uptake by SMC and SMP were increased from 5.73 to 27.59 mg/g and 5.55 to 24.93 mg/g, respectively. As presented in Fig. 5, a negative relationship was observed between the removal efficiency and adsorption capacity. Therefore, the removal efficiency of nitrate for both adsorbents decreased with increasing the sorption capacity of the sorbent. On the other hand, for a given mass of the sorbent, the adsorption capacity was increased with an increase in nitrate concentration due to the adsorption of more amounts of substances per unit mass.

3.6. Regeneration of sorbents

The regeneration and reuse of the adsorbent regarding the cost of water and wastewater treatment is an important parameter must be noticed. A major advantage of modified adsorbents is their ability to preserve their functionality in the adsorption process even after several times of regeneration/reuse cycles.

Fig. 6 shows the reduction in adsorption performance from 95 to 75 and 90 to 68 for SMC and SMP for the first to 5th reuse cycles, respectively. In other words, the sorption efficiency was decreased by increasing the regeneration cycles. After the first cycle of regeneration, a sorption efficiency of 95% was observed for both sorbents. Then, the nitrate removal efficiency was gradually decreased in the sequence of cycles and after the fifth cycle; the removal efficiency was reached to 75% for SMC and 68% for SMP. Results revealed that SMC has a better regeneration capability in comparison with SMP with a lost less than 20% of regeneration efficiency after 5 cycles of regeneration. This may be due to its high structural stability and physicochemical properties for its internal and external structures [48].

3.7. Adsorption isotherms and kinetics

As discussed earlier, adsorption isotherm models were used to define the equilibrium behavior between adsorbate molecules and the sorbent's surface. The values of isotherm parameters are summarized in Table 4. Langmuir isotherm model found to be the best model describing the nitrate sorption with the coefficients of determination of 0.98 and 0.99

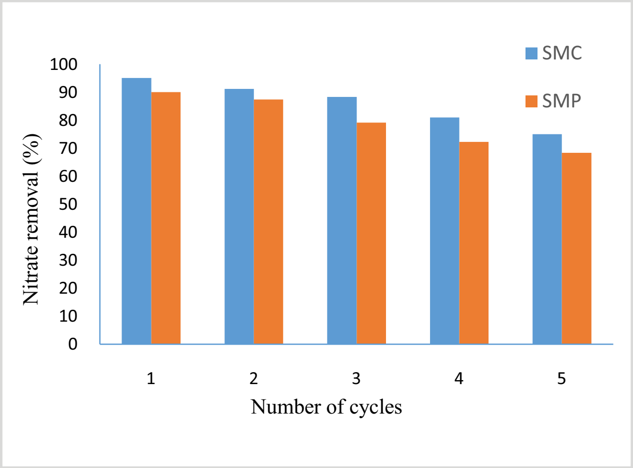

Fig. 6. Effect of regeneration cycles on nitrate removal efficiency.

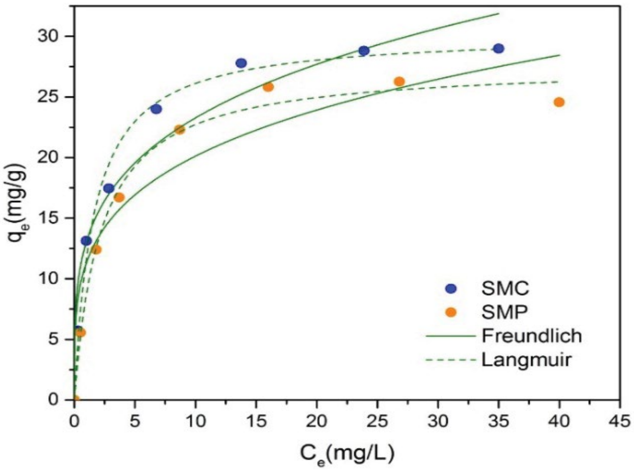

Fig. 7. Isotherm models.

for SMC and SMP, respectively. Langmuir isotherm implied that the adsorption follows a monolayer sorption assumption. The estimated monolayer sorption capacity of SMP (27.6 mg/g) was less than that for SMC (30.2 mg/g) for nitrate. Also, the value of R_L and n for SMC and SMP were 0.052, 3.98 and 0.078, 4.00, respectively, confirming favorability of both Freundlich and Langmuir models for the sorption of nitrate by sorbents.

The kinetic model and calculated the kinetic parameter of nitrate adsorption by SMC and SMP under optimal conditions are shown in Table 5 and Fig. 8. As shown in Table 5, for both sorbents, the pseudo-first-order model (R^2 = 0.98 for SMC and R^2 = 0.97 for SMP) found to be the best descriptive model.

The nitrate adsorption on SMC and SMP was compared with various other adsorbents [18,49–58]. As shown in Table 6, in most studies, the Langmuir model was found to fit well with the data. Also, nitrate sorption by different adsorbents is characterized by the pseudo-second-order model. It can be seen that both adsorbents have comparable

Table 4
Nonlinear-estimated parameters of isotherm models

Sorbent	Model	Parameter	Value	Standard error	Adj. R^2
SMC	Freundlich	k_f (mg/g(L/mg)$^{1/n}$)	13.058	1.380	0.948
		n	3.984	0.599	
	Langmuir	q_m (mg/g)	30.260	0.828	0.989
		b	0.630	0.084	
SMP	Freundlich	k_f (mg/g(L/mg)$^{1/n}$)	11.320	1.646	0.914
		n	4.004	0.805	
	Langmuir	q_m (mg/g)	27.661	0.772	0.990
		b	0.460	0.059	

Table 5
Nonlinear-estimated parameters of kinetic models

Sorbent	Model	Parameters	Values	Standard error	Adj. R^2
SMC	Pseudo-second-order	k_2 (mg/g min)	0.006	0.002	0.951
		q_e (mg/g)	14.649	0.708	
	Pseudo-first-order	k_1 (1/min)	0.069	0.006	0.985
		q_e (mg/g)	13.256	0.270	
SMP	Pseudo-second-order	k_2 (mg/g min)	0.005	0.002	0.940
		q_e (mg/g)	14.395	0.857	
	Pseudo-first-order	k_1 (1/min)	0.059	0.007	0.976
		q_e (mg/g)	12.792	0.359	

Table 6
Adsorption isotherms, kinetic studies and other parameters of various adsorbents used for nitrate removal

Adsorbent	Optimum pH	Isotherm model	Kinetic model	q_{max} (mg/g)	References
Cross-linked chitosan beads	5	Langmuir	–	90.7	[18]
Modified beet residue	–	Langmuir	Pseudo-second-order	78.74	[49]
Nano-alumina	4.4	Langmuir	Pseudo -second-order	5.48	[50]
Surfactant modified zeolite (SMZ)	6	Langmuir-Freundlich-Dubinin-Redushkevich	Pseudo-second-order	9.36	[16]
Nano-alumina/Iron-modified	5	Langmuir	Pseudo-second-order	70.8	[51]
Pumice (IMP)	5	Langmuir	Pseudo-second-order	70.8	[51]
Clay	5.1	Langmuir	Pseudo-first-order	244.06	[52]
Granular chitosan-Fe^{3+} complex	–	Langmuir, Freundlich, Dubinin–Radushkevich	Pseudo-second-order	8.35	[53]
Modified pine sawdust	6.5	Redlich-Peterson, Langmuir	–	32.8	[54]
Modified sugarcane bagasse biochar	2	Langmuir	Pseudo-second-order	28.21	[55]
Modified granular activated carbon	5	Langmuir	Pseudo-second-order	21.51	[56]
Biochar-supported nano zero-valent iron	8	Langmuir	Pseudo-first-order	–	[57]
Natural Pumice	3	Freundlich	–	164.37	[58]
Modified clinoptilolite	5	Langmuir	Pseudo-first-order	30.26	This study
Modified pumice	5	Langmuir	Pseudo-first-order	27.66	This study

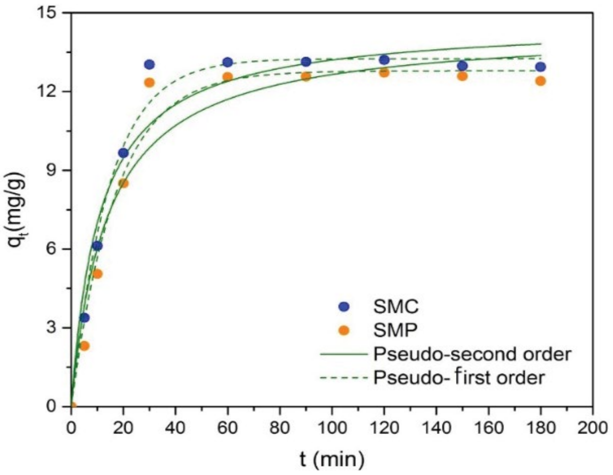

Fig. 8. Kinetic models.

adsorption efficiency with the other adsorbents based on their maximum adsorption capacity for nitrate removal from aqueous solutions.

4. Conclusions

In the present work, SMC and SMP were used as low-cost and efficient adsorbents with a considerable capacity for nitrate removal. Following conclusions could be remarkable:

- The compositional structure of SMC and SMP were found to be near the natural zeolites.
- The textural and internal analysis of sorbents showed that specific surface area of SMC could be decreased after modification but it could not be the case for SMP.
- The adsorption process was found to be highly depended on pH and initial nitrate concentration.
- The optimal condition for nitrate sorption observed in acidic pH (pH = 5), 30 min contact time and 0.5 g/L adsorbent dosage.
- SMC and SMP adsorbents can retain their sorption capacity for nitrate even after several cycles of regeneration.

The results showed that SMC and SMP both have a considerable sorption capacity for nitrate and they could be considered as effective and not expensive adsorbents for the removal of nitrate from aqueous environments.

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